Etching Techniques for Gold-Containing Ag_3Sn Alloys and Amalgams*

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Argon-ion etching and various other chemical etchants were applied to conventional and gold-containing dental alloys and amalgams. The polished and etched specimens were studied by optical and/or electron optical methods and by energy-dispersive x-ray spectroscopy. Chemical etchants, though effective, have the disadvantage of accentuating surface scratches. This, in turn, causes difficulty in the accurate determination of microstructure. Argon-ion etching, on the other hand, was found to clearly reveal microstructural details as well as minute features of the solidification process. Any surface irregularities in this case were not revealed. Although argon-ion etching was successful for the conventional and the gold-containing Ag_3Sn annealed alloys, it caused sufficient specimen heating to drive off high-vapor-pressure mercury compounds and hence was unsuitable for amalgams. A double cyanide chemical etchant was found to clearly reveal γ grains and matrix phases γ_1 and γ_2 in the conventional amalgam but revealed only γ grains and (Au–Sn) rings surrounding the γ grains in the gold-containing amalgam. After further etching in 30% nitric acid, the gold-containing amalgam revealed γ_1 and Au–Sn phases between the boundary regions of the γ grains.

Nomenclature. The following Greek letter notation used in this paper to represent different phases in a conventional amalgam has been commonly accepted in the dental literature. γ (unreacted Ag_3Sn particles) represented by *A*. γ_1 (Ag_2Hg_3) represented by *B*. γ_2 ($Sn_{7-8}Hg$) represented by *C*. Au–Sn ($AuSn_4$) rings surrounding the γ particles represented by *D* and light areas between the boundary regions of the γ particles represented by *E*.

Introduction

Silver–tin amalgams containing small amounts of copper and zinc have been widely used for years as dental restorative materials. More

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recently, gold has been substituted in varying amounts in the basic Ag_3Sn structure in an effort to develop a better dental alloy and an amalgam which might be free of the γ_2 phase [1,2]. Metallographic etching techniques which show up the various phases present in the alloy and in the amalgam have been developed from time to time and reported in the literature [3–9]. This paper reports on the various techniques of metallographic etching used to delineate the different phases and other microstructural features present in conventional and gold-containing alloys and in amalgams prepared from these alloys.

Etching Procedures

Microstructural features of a metal or an alloy have most generally been revealed by using a chemical reagent which selectively etches and/or stains different grains or other constituents. Preferential attack may occur as a result of (1) differences in chemical composition in different phases, (2) orientation differences, and (3) differences in the etching of grain boundaries, dislocations, or other defects at the surface. Recently, positive-ion bombardment or sputtering techniques have also been used to reveal structural characteristics of many complicated alloy systems. In the present investigation both chemical reagents and ion-beam sputtering techniques have been used. It is essential, of course, that the sample be well polished mechanically prior to etching. Such polishing is really a fine art and usually requires considerable experience, particularly with multiphase alloys containing both hard and soft constituents, to minimize artifacts due to deep scratches, smearing of soft components, excessive cold work or phase changes resulting from heating during sample preparation. Polishing techniques to minimize or eliminate such artifacts have been described in the literature and will not be discussed here.

A number of chemical reagents for the etching of amalgam alloys of silver and tin containing varying amounts of copper and/or zinc have been reported previously. Murphy [3] found that electrolytic etching of alloys of silver and tin in a 1% hydrofluoric acid solution gave good results. Crowell [4], however, found that it was difficult to obtain evenly etched, unstained samples with this etch when the alloy contained 1% or more copper. He proposed a new chemical etchant for the Ag–Sn–Cu system as follows: $K_2Cr_2O_7$, 2 g; NaF, 1 g; H_2SO_4 (concentrated and a specific gravity of 1.84), 3 ml; distilled H_2O, 100 ml. To the above solution a small amount of sodium chloride was added. This solution

etched Ag–Sn–Cu–Zn alloys but the surface of the specimen was covered with a thin black film of silver chloride which was removed either by sodium thiosulfate or by ammonia before the structure was revealed for microscopic examination. Etching proceeded at a moderate rate and took about 30 sec at ambient temperature. This etching procedure was also applied to the Ag–Sn–Au system in the present case.

For amalgams several etchants have been proposed. Smith et al. [5] studied both electrolytic and chemical etchants. In the electrolytic technique, they used a Cenco Hangosky electrolytic polishing and etching machine. The electrolyte used was the standard nonferrous electrolyte supplied with the equipment. In the chemical etching technique, they immersed a hardened dental amalgam in a 30% nitric acid solution. The time required to etch the specimen surface in the nitric acid solution seemed to depend on the mercury content; the higher the mercury content, the larger the time required to develop the structure. The structure revealed was essentially the same in both cases. The major disadvantage of these methods was that the matrix phases were not clearly distinguished from each other.

Allan et al. [6] developed a new chemical etchant to reveal different phases in dental amalgam. The first solution was made from 4 g of $K_2Cr_2O_7$ and 1 g of KI mixed in 100 ml of distilled H_2O. The second solution was made from 4 g of iodine to which 96 ml of ethyl alcohol was added. The two solutions were used in order for prescribed intervals and then the surface was rinsed in hypo solution ($Na_2S_2O_3 \cdot 5H_2O$ dissolved in water). This etchant revealed all the required phases in dental amalgam as demonstrated by the authors.

Otani [7] also produced an etched surface showing good microstructural detail by storing relief-polished amalgam specimens separately with a small amount of mercury in a tightly closed container at 60°C for a few hours. However, this etching procedure is not commonly used.

Wing [8] investigated a series of chemical and electrolytic etchants for dental amalgam and found that the acid etching solutions showed artifacts which were likely to be confused with the reaction products. He proposed a double cyanide etch technique which was made up of an initial solution consisting of 8% potassium cyanide to which was added 1 g of iodine per 25 ml of solution. A second solution, in which the specimen was simply immersed, consisted of equal parts of 10% ammonium hydroxide and 10% potassium ferric cyanide. The above double cyanide etchant resolved both matrix phases γ_1 and γ_2 in an amalgam. In the present investigation of the microstructure in the gold-containing amalgam Wing's [8] double cyanide etchant was found to clearly reveal γ grains and Au–Sn rings surrounding the grains while the

matrix phases showed good structure only when further etched in a 30% nitric acid solution.

Obviously, even good mechanical polishing procedures leave fine scratches on the specimen surface which may be accentuated on chemical etching. To minimize this effect, a new etching technique using argon-ion bombardment has been applied to Ag–Sn–Au alloys and amalgams [9]. Under carefully controlled conditions of gas pressure, low ion-beam angle with respect to the surface, and rotation of the specimen about an axis perpendicular to its surface, excellent etching of the surface results. This technique gave very good results in the conventional and in the gold-containing Ag_3Sn alloys but was a complete failure in the case of amalgams where deep pitting was produced on the surface, apparently due to the heating of the sample by the ion-beam, and the high vapor pressure of the mercury compounds in the amalgam. Similar etching experiments carried out with a liquid-nitrogen cold stage for the specimen holder showed similar results. A more efficient cooling stage might improve the results for amalgams.

Results and Discussion

The results of these experiments are shown most clearly by reference to the photomicrographs in Figs. 1–8.

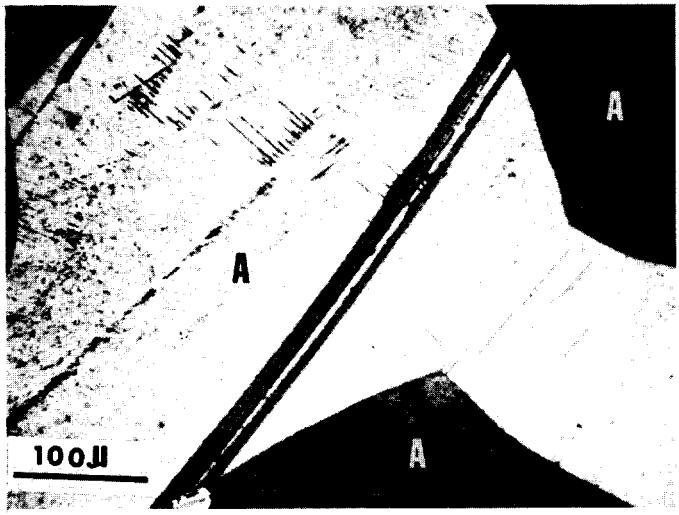

FIG. 1. Optical photomicrograph of a pure Ag_3Sn annealed alloy surface after being polished mechanically and etched using Crowell's solution [4], showing clearly grain structure (marked *A*) with sharp grain boundaries and also deformation twins along scratches.

The most satisfactory chemical etchant for showing up the detailed microstructure of the surface of a mechanically polished homogeneous Ag_3Sn annealed alloy was considered to be Crowell's etchant [4], as shown in Fig. 1. The grain structure (areas marked *A*), grain boundaries, and deformation twins are sharply delineated, but some scratches are also strongly enhanced. The twins observed are, in fact, artifacts produced along scratches by the deformation during mechanical polishing. Figure 2 shows a higher magnification scanning electron photomicrograph of the same specimen after mechanical polishing and etching by argon-ion bombardment. Microstructural details (arrow-type structure formed within some grains during solidification) are clearly revealed. No evidence of mechanical polishing scratches are seen. Energy dispersive x-ray analysis confirmed the homogeneity of this alloy.

Crowell's etchant [4] was also found to be the most satisfactory chemical etchant for the Ag_3Sn alloy in which up to 15% gold was substituted for silver. Differential contrast between the grains was not as great as for pure Ag_3Sn, but grain boundaries were clearly defined as dark lines in the optical photomicrograph. Figure 3 shows a typical optical photomicrograph of the 15% gold-containing Ag_3Sn annealed alloy where part of the large γ phase grains (marked *A*) are separated

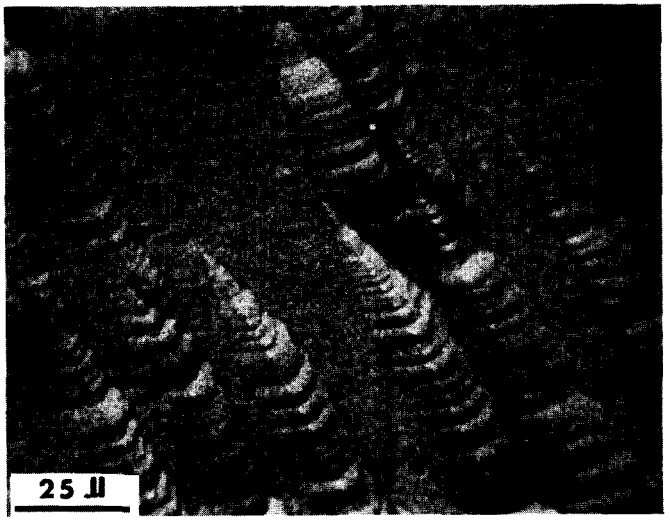

FIG. 2. A scanning electron photomicrograph of a pure Ag_3Sn annealed alloy surface after being polished mechanically and then etched by argon-ion bombardment, showing arrow-type structure within the grain formed during solidification process and no evidence of scratches produced by mechanical polishing.

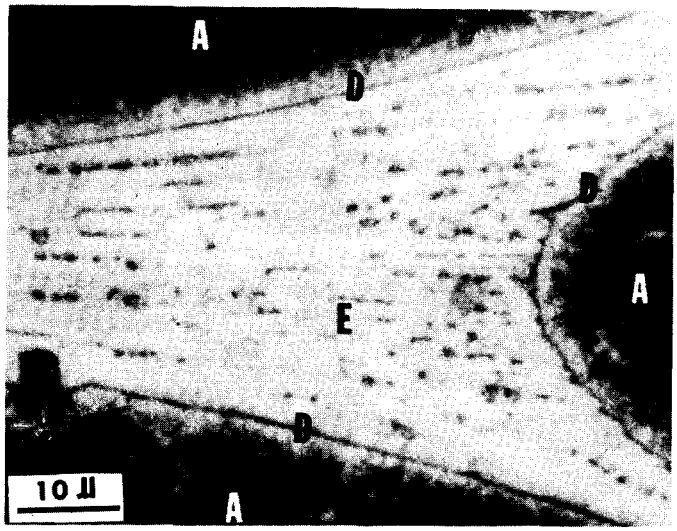

FIG. 3. An optical photomicrograph of a 15% gold-containing Ag_3Sn annealed alloy surface after being polished mechanically and then etched using Crowell's solution [4]. Part of large size γ grains (marked *A*) are separated by boundary regions *E* and dark rings *D*, both corresponding to second Au–Sn phase.

from a second-phase material (marked *E*) which was identified as a gold–tin phase, $AuSn_4$ [10]. The dark rings (marked *D*) around the border of this second phase appear as white rings in the scanning electron microscope and also correspond to an Au–Sn phase, as confirmed by energy-dispersive x-ray analysis. Figure 4 shows a typical scanning electron photomicrograph of the same alloy specimen after mechanical polishing followed by argon-ion bombardment. Differential contrast between the grains marked *A* is good enough to predict their different orientations. No significant contrast difference exists between some of the grains (marked *A*) and boundary regions (marked *E*) of the grains. These boundary regions correspond to the Au–Sn phase, as confirmed by energy-dispersive x-ray analysis. However, grains and boundary regions between the grains are well separated by sharp boundaries as white rings (marked *D*) corresponding to the (Au-Sn) phase, as stated earlier. Dark areas around the white rings are characteristic of pits produced by the etchant. Other microstructural details such as twins are vividly defined in this scanning electron photomicrograph.

The amalgams were, in general, more difficult to etch satisfactorily. As expected, Wing's double cyanide etching procedure [8] gave an excellent etch for the conventional Ag_3Sn amalgam after mechanical

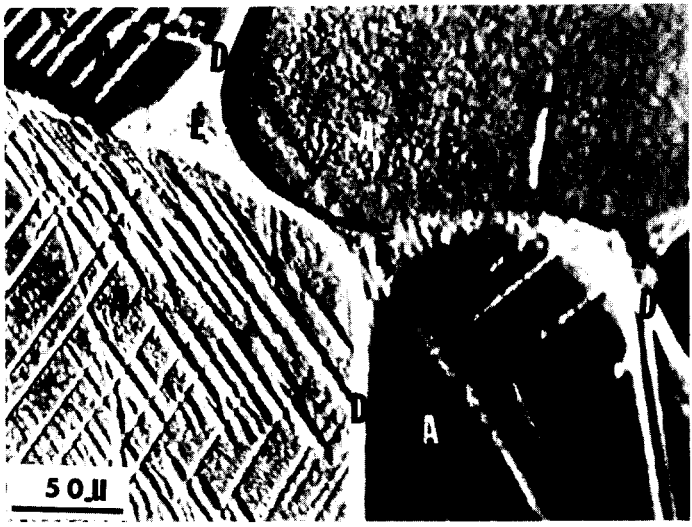

FIG. 4. A scanning electron photomicrograph of a 15% gold-containing Ag_3Sn annealed alloy surface after being polished mechanically and then etched by argon-ion bombardment. Particles of γ phase *A* containing some gold are separated by their boundary regions *E* and also by white rings *D* of second Au–Sn phase. Microstructural features such as deformation twins produced by mechanical polishing are clearly observed.

polishing, as shown in Fig. 5. The moderately dark areas (marked *A*) show unreacted spherical γ-phase particles and the light areas of matrix between these particles (marked *B*) correspond to the $\gamma_1(Ag_2Hg_3)$ phase. The dark areas, such as marked *C*, are the $\gamma_2(Sn_{7-8}Hg)$ phase. The etching behavior in this double cyanide etchant develops an optical contrast which serves nicely to delineate these phases in the metallograph. These phases were further confirmed by energy-dispersive x-ray analysis.

The microstructural details of the amalgam made from a spherical silver–tin alloy with 15% gold were partially revealed by the same double cyanide etchant [8]. This amalgam is apparently a three-phase system (assuming the γ_2 phase is eliminated, as confirmed by x-ray diffraction results), although the phases are not obvious in the optical photomicrograph shown in Fig. 6, without additional information from energy-dispersive x-ray analysis. The large-size spherical particles marked *A* are unreacted γ phase Ag_3Sn particles containing some gold. The moderately dark gray rings marked *D* surrounding each of these particles were found to correspond to Au–Sn phase. Oddly enough, little or no mercury was found in the γ particles inside the Au–Sn ring. This

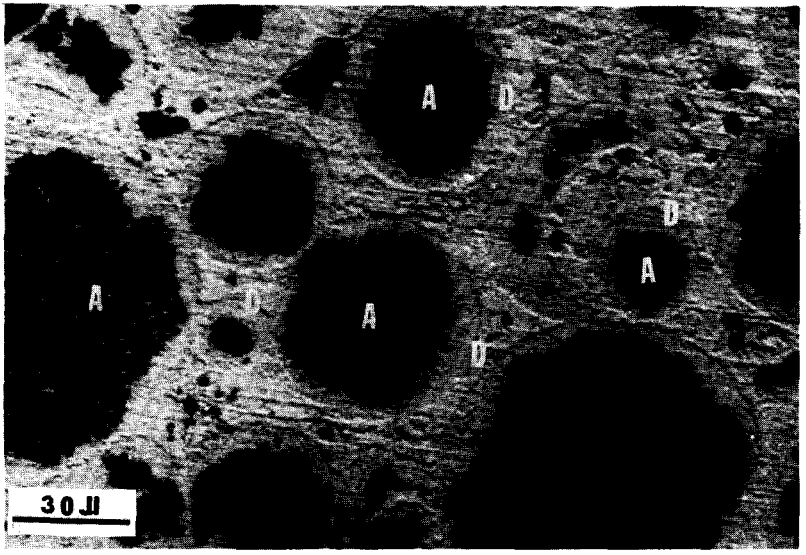

FIG. 5. An optical photomicrograph of a pure Ag_3Sn amalgam surface after being polished mechanically and then etched using Wing's double cyanide solutions [8]; showing γ, γ_1, and γ_2 phases marked by areas *A*, *B*, and *C*.

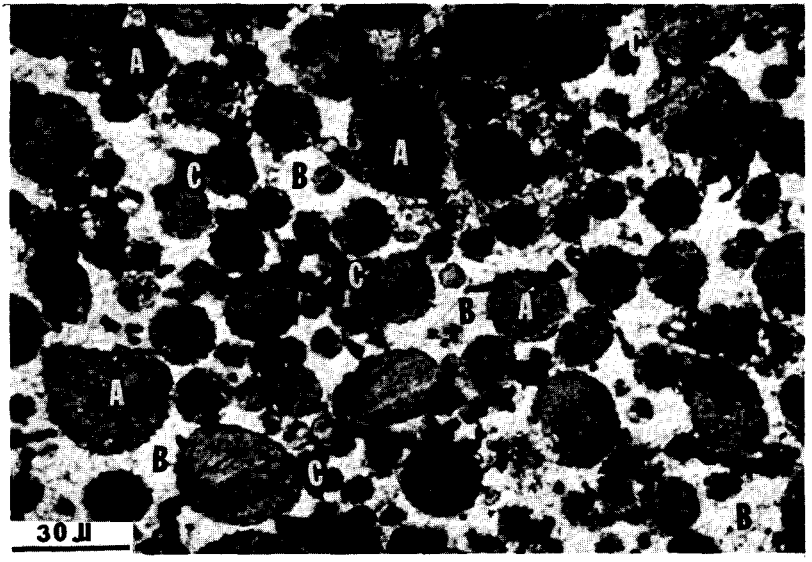

FIG. 6. An optical photomicrograph of a 15% gold-containing amalgam surface after being polished mechanically and then etched using Wing's double cyanide solutions [8]. Dark rings of Au–Sn phase marked *D* are surrounding the γ grains marked *A*. Dendritic structure is clearly revealed within the grains.

suggests the necessary outward diffusion of silver and tin to react with mercury and form matrix phases. Moreover, the matrix phases in the gold-containing Ag_3Sn amalgam did not show up very well by the double cyanide etchant. Further etching of the surface in a 30% nitric acid solution revealed other phases more clearly. Figure 7 shows a typical scanning electron photomicrograph showing dark pits (marked *B*) where the γ_1 phase has been removed by the etchant. No γ_2 phase could be seen, as expected for this amalgam. The other phases such as the γ phase (marked *A*), and the (Au–Sn) phase (areas *E* between the boundary regions of the grains and also areas *D* as white rings surrounding the grains) are shown in this photomicrograph.

Attempts to etch the amalgam samples by argon–ion bombardment were completely unsatisfactory, due to the development of many pits on the specimen surface. This pitting is the result of heating by the ion beam which, with the high vapor pressure of the mercury-containing phases, caused the almost complete removal of mercury from the surface layers. Figure 8 shows an optical photomicrograph of the 15% gold-containing amalgam surface after ion bombardment. Although γ

FIG. 7. A scanning electron photomicrograph of a 15% gold-containing amalgam surface after being polished mechanically and etched in this order, first using Wing's double cyanide solutions [8] and then using a 30% nitric acid solution. Dark pits (marked *B*) show that γ_1 phase is removed by the nitric acid etchant. White rings marked *D* and boundary regions of γ grains marked *E* both correspond to Au–Sn phase.

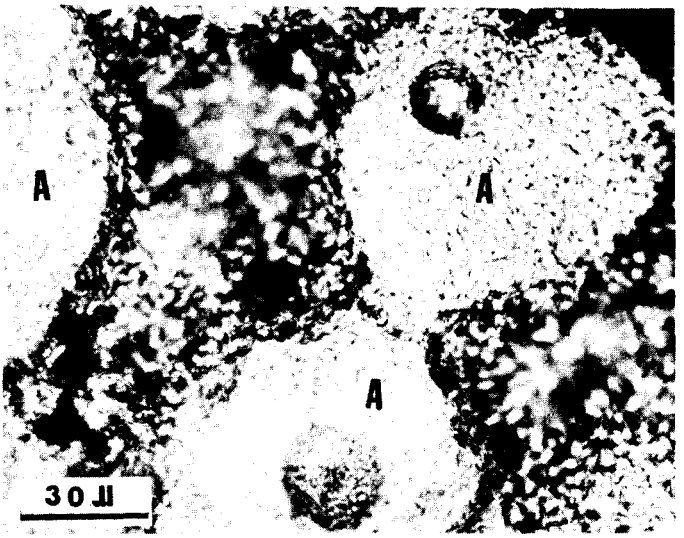

FIG. 8. An optical photomicrograph of a 15% gold-containing amalgam surface after being polished mechanically and then etched by argon-ion bombardment, showing surface damage caused from the removal of mercury atoms. The grains *A* are identified as γ grains containing some gold.

grains (marked *A*) are easily identified from the photomicrograph, other phases are not evident due to surface damage produced during ion bombardment caused by heating. Preliminary attempts at cooling the sample with liquid nitrogen during ion bombardment have not yet proved completely satisfactory, and additional investigations are needed.

Summary

Both chemical and ion-beam etching techniques have been investigated for conventional Ag_3Sn dental alloys, for spherical dental alloys containing 15% gold substituted for silver, and for amalgams of both these alloys. Both etching techniques, chemical and argon-ion bombardment, were found to be satisfactory for revealing the various phases and other microstructural details present in the dental alloys. Crowell's etchant [4] was generally found to be the best chemical etchant. For both of these alloys, ion-beam etching was found to be even more useful than chemical etching because fewer artifacts were produced. For amalgams it was found that ion-beam etching was completely unsatisfac-

tory because of the removal of mercury and the development of pits on the surface. Wing's double cyanide etchant [8] followed by 30% nitric acid etch was found to be most satisfactory for the gold-containing amalgams.

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